Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries

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HIGHLIGHTS

► We report an ultrasonic-assisted hydrometallurgical technique.
► Ascorbic acid is chosen as both leaching reagent and reducing agent.
► This technique avoids use of the traditional reducing agent H_2O_2.
► Leaching efficiencies are as high as 94.8% for Co and 98.5%.
► The acid leaching reaction mechanism has been preliminarily studied.

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ABSTRACT

Recycling of the major components from spent Li-ion batteries (LIBs) is considered desirable to prevent environmental pollution and recycle valuable metals. The present work investigates a novel process for recovering Co and Li from the cathode materials (containing $LiCoO_2$ and Al) by a combination of ultrasonic washing, calcination, and organic acid leaching. Copper can also be recovered from the anode materials after they are manually separated from the cathode. Ascorbic acid is chosen as both leaching reagent and reducing agent to improve the Co recovery efficiency. Leaching efficiencies as high as 94.8% for Co and 98.5% for Li are achieved with a 1.25 mol L^{-1} ascorbic acid solution, leaching temperature of 70 °C, leaching time of 20 min, and solid-to-liquid ratio of 25 gL^{-1}. The acid leaching reaction mechanism has been preliminarily studied based on the structure of ascorbic acid. This method is shown to offer an efficient way to recycle valuable materials from spent LIBs, and it can be scaled up for commercial application.

1. Introduction

Lithium-ion batteries (LIBs) are extensively used as electrochemical power sources in electronic equipment (for instance, cellular phones, notebook computers, and video cameras) and in electric vehicles, because of their high power and energy density, high cell voltage, long storage life, low self-discharge rate, and wide operating temperature range [1,2]. The continuous growth in the use of such portable devices has greatly stimulated the production and consumption of lithium-ion batteries. However, vast quantities of chemical substances (including copper, aluminum, lithium, cobalt, manganese, and organic electrolytes) will be produced as waste after the lifetime failure of the LIBs. If the spent batteries are simply disposed by dumping them in landfill, soil contamination resulting from the leakage of organic electrolytes as well as heavy metals in the batteries will become a serious environmental concern. In addition, the available dumping sites for disposal are limited in number and very costly [3–6]. Therefore, the recycling of the major components from spent LIBs is considered to be highly desirable to prevent environmental pollution and provide alternative sources of lithium, cobalt, copper, etc.

The goal is to recover the valuable materials contained in the spent LIBs in the form of pure compounds ready to be used in the manufacture of new batteries, thus achieving a "true" recycling of these batteries. At the bench scale, research has focused on hydrometallurgical methods for the recovery of valuable components from spent LIBs. Compared to a pyrometallurgical approach, which typically involves the emission of toxic gases and consumption of intensive energy, the hydrometallurgical approach is more favorable from an environmental viewpoint. In a typical

hydrometallurgical approach, both physical and chemical processes are normally included in the material recovery process [7,8]. Physical processes are used as a pretreatment step and mainly involve mechanical, mechanochemical, dissolution, and thermal processes. Chemical processes consist of acid-, base- or bio-leaching; solvent extraction; chemical precipitation; electro-chemical reaction; and re-synthesis of electrode and other reactive materials.

Recovery of metals from spent LIBs has been reported to have been attained by solvent extraction using di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis-(2,4,4-tri-methyl-pentyl) phos-phinic acid (Cyanex 272), trioctylamine (TOA), diethylhexyl phosphoric acid (DEHPA), and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) [9–12]. Chemical precipitation with NaOH, NH_4OH, citric acid, and ammonium oxalate were also reported to form $Co(OH)_2$, cobalt oxalate, and lithium oxalate [13–17]. Acid leaching plays a key role in all of the chemical processes reported above. Several strong acidic media such as H_2SO_4, HCl, and HNO_3 have been tested to dissolve Li and Co in electrode materials [18–21]; however, they also introduce significant secondary pollution, for instance, toxic gases emission. To eliminate such secondary pollution, we have sought a replacement of these strong acids without sacrificing high leaching efficiency.

Organic ascorbic acid is a naturally occurring organic compound that behaves as a vinylogous carboxylic acid as well as a mild reducing agent. Ascorbic acid has been industrially produced for around 70 years. Most of the commercially manufactured ascorbic acid is synthesized via the conventional seven-step Reichstein process. In order to increase process efficiency and reduce capital costs, biotechnological approaches for ascorbic acid production have been investigated recently [22,23]. The latest data about production of ascorbic acid showed the global production capacity of ascorbic acid reached more than 130,000 tons per year at present [24]. In this study, we have designed and tested an ultrasonic-assisted hydrometallurgical technique using ascorbic acid as leaching reagent and reducing agent for recovery of cobalt and lithium from spent LIBs.

2. Experimental

2.1. Materials and reagents

All reagents used in this study were analytical grade, and all the solutions were prepared with specified concentrations in distilled water. The cylindrical spent LIBs used in mobile phones and laptops from different manufacturers and with different sizes were collected from the Beijing Institute of Technology. Aqua regia (HCl:HNO_3 in 3 to 1 ratio) was used to completely digest the spent $LiCoO_2$ powder extracted from the cathode at 90 °C in order to analyze the Co and Li contents. Ascorbic acid solution with different concentrations was used for the leaching process. In the pretreat-ment, ultrasonic-assisted *N*-methyl-2-pyrrolidone (NMP) was used to separate the cathode active materials from the aluminum foil.

2.2. Experimental procedure

The spent LIBs were first discharged to prevent short-circuiting and self-ignition. The cylindrical cells were then removed from the spent LIBs, and were subjected to the following main procedures.

(a) Dismantling and anode/cathode separation: The spent LIBs were manually dismantled to remove the plastic and steel cases, and the anodes and cathodes were uncurled and separated. Then, the cathode foils were cut into very small parts using a scissors.

(b) NMP immersion and thermal treatment: The cathode parts were immersed in NMP in an ultrasonic washing container for 20 min with an ultrasonic frequency of 40 Hz and electric power of 100 W. The ultrasonic treatment was intended to improve the efficiency and yield of separating the cathode active materials from the aluminum foils. After filtration and drying, the spent $LiCoO_2$ powders were roasted at 450 °C for 1 h to burn off impurities, such as carbon and polyvinylidene fluoride (PVDF) binder. The powders were then ground for 30 min in a planetary ball mill to obtain smaller particles with higher surface to increase leaching efficiency.

(c) Ascorbic acid leaching: The separated lithium cobalt oxide powder and ascorbic acid solution were placed in a three-necked and round-bottomed thermostatic Pyrex reactor with 100 mL volume, which was placed in a water bath to control the reaction temperature during the leaching. The reactor was fitted with an impeller magnetic stirrer and equipped with a vapor condenser to reduce the loss of water by evaporation. In the ascorbic acid leaching, the following operational variables were investigated: temperature (30–90 °C), duration (5–50 min), concentration of ascorbic acid (0.3–1.5 molL^{-1}), and solid/liquid (*S/L*) ratio (15–50 gL^{-1}). The mixing speed was set at 300 rpm. After leaching, the resulting solution and insoluble residue were separated by filtration and washed with distilled water, yielding a pink filtrate and a black residue.

2.3. Analytical methods

Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine the appro-priate calcination temperature of the heat treatment.

After the digestion of the $LiCoO_2$ powder sample, the total amounts of Co and Li were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The amounts of cobalt and lithium in the resulted leaching solution were also measured by atomic absorption spectrophotometry (AAS) to obtain the leaching efficiency at different stages. The leaching efficiency is defined as the ratio of the amount of a chemical species in the leachate to the total amount of that species in the original cathode.

In-situ X-ray diffraction (XRD) was carried out during calcina-tion of the samples at Sector 11 of the Advanced Photon Source (APS) at Argonne National Laboratory. The X-ray wavelength was pre-set to 0.107805 Å (fixed wavelength for this station). The high-energy X-ray source at about 0.1 Å provides excellent penetration for the detection of structural changes in the bulk part of the samples. The high flux of the X-ray beam at APS is a major advan-tage in carrying out fast experiments at one spectrum per minute. After being separated from the aluminum foil, the cathode material was pressed into pellets about 2 mm in thickness. Each pellet was then placed vertically in a programmable furnace with glass windows. The sample was heated up to 900 °C with a heating rate of 10 °C per minute under air. During the temperature-programmed heating, a high-energy X-ray hit the sample hori-zontally (see Fig. 1), and a 2D X-ray detector was used to collect the XRD profiles employing a transmission mode with a speed of one spectrum per minute. The collected 2D pattern was then integrated into conventional 1D data (intensity vs. 2q) for the final data analysis.

Scanning electron microscopy (SEM, Hitachi S-570) combined with energy dispersive X-ray spectroscopy (EDX) was used to analyze the morphology of the spent $LiCoO_2$ and the leaching residues. To further study the mechanism of the reaction, Materials
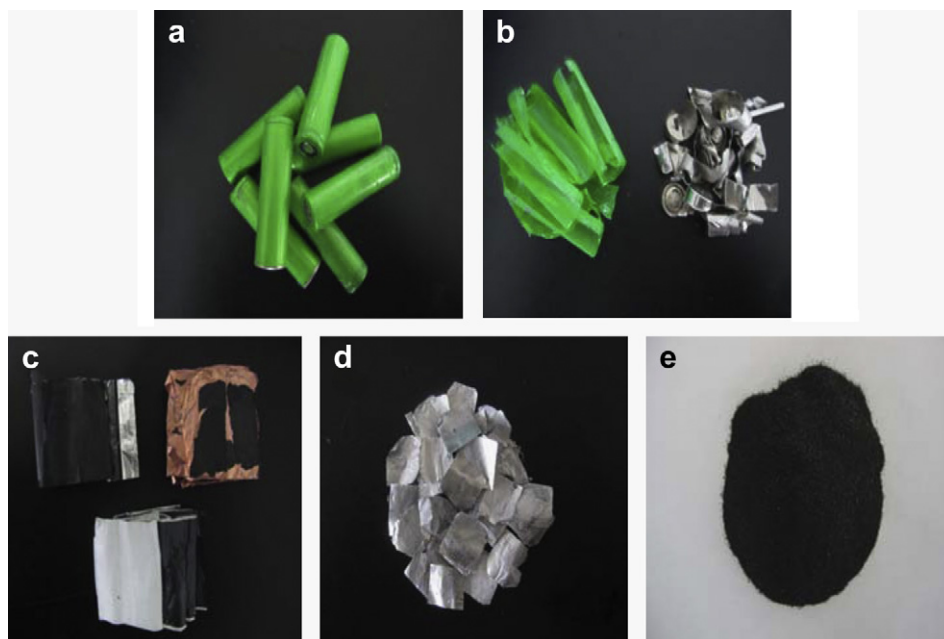
Fig. 1. Illustrations of different parts dismantled from spent Li-ion batteries: (a) spent Li-ion batteries, (b) plastic and metallic shells, (c) cathode, anode and separator, (d) Al foils after immersion in NMP, and (e) the active materials after filtration and drying.

Studio (Accelrys Enterprise Platform) was used to calculate and simulate the molecular structure of the possible products of the leaching reaction of waste $LiCoO_2$ with ascorbic acid.

3. Results and discussion

3.1. Pretreatment of spent LIBs

The spent LIBs were dismantled and separated manually into different parts, shown in Fig. 1. The plastic and metallic shells from the cells (Fig. 1b) were recovered easily and completely. After the dissolution of the binder (PVDF) by immersing the cathode in NMP, the active material was separated from the aluminum foils. To increase the efficiency and yield of separating the cathode active materials from the aluminum foils, an ultrasonic treatment was introduced. The recovered Al foil and separated active materials are shown in Fig. 1d and e. Little cathode material was left on the

aluminum foil after the pretreatment, and the aluminum foil was in good shape without any damage.

The separated active materials (the spent $LiCoO_2$ powder) were heated from 20 to 1000 °C using the TGA/DSC analyzer with a heating rate of 10 °C min^{-1} in an air atmosphere. Three distinct regions of weight loss were observed (20—275 °C, 275—700 °C, and 700—1000 °C), as shown in Fig. 2 and Table 1. A weight loss of 1.0 wt % was detected from room temperature to 275 °C, with a corresponding endothermic DSC peak at 275 °C, which resulted from the loss of bound water in the materials. From 275 to 700 °C, the total weight loss of 3.2 wt% was associated with several exothermic DSC peaks at the temperature range, which likely correspond to the burning of the acetylene black and the decomposition of residue of the binder (PVDF). The significant exothermic DSC peak at 850 °C with a weight loss of 1.5 wt% in the temperature range of 700—1000 °C indicated a phase change of $LiCoO_2$ and the loss of lithium at high temperature.

Fig. 3 shows the in-situ XRD patterns of the cathode active materials during calcination to 900 °C. In the sample before calcination, all the diffraction peaks were indexed to $LiCoO_2$, Co_3O_4, and C. The carbon in the sample likely came from the graphite in the anode, which became mixed into the cathode materials during battery dismantling, as well as from the conductive agent in the cathode material. A small amount of Co_3O_4 was also detected in the initial sample, which is believed to be due to the transformation of $LiCoO_2$ because of the release of HF from the batteries during usage [25]. When the temperature reached about 700 °C, the absence of carbon in the XRD pattern indicated that it had burned off. The rest
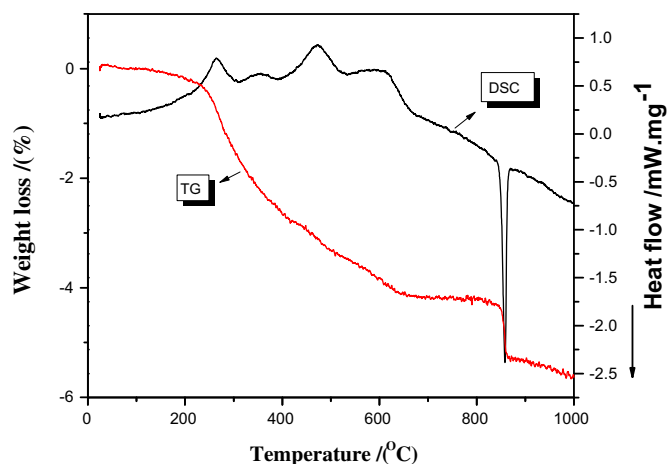

Fig. 2. TGA/DSC curves for the spent cathode materials.

Table 1
TGA data for cathode materials.

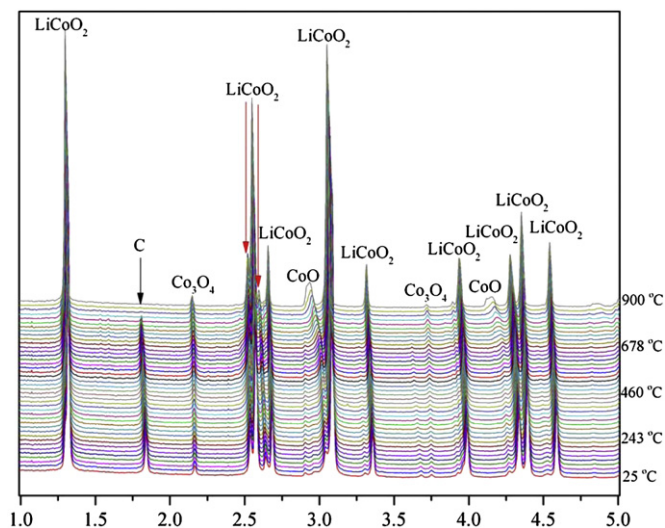|	20—275 °C	275—700 °C	700—1000 °C
Weight loss (wt%)	0.98	3.2	1.45
Assignment	Loss of bound water	Burning of acetylene black and decomposition of PVDF	Phase change of $LiCoO_2$ and the loss of lithium

Fig. 3. In-situ XRD patterns of the samples during heat treatment from room temperature (bottom) to 900 °C (top).

Fig. 5. EDX spectroscopy of the leach residues.

of the material in the sample was identified as $LiCoO_2$ and Co_3O_4, Further increasing the temperature to 900 °C led to the formation of CoO from either $LiCoO_2$ or Co_3O_4, which is consistent with the DSC/TGA results. According to the TGA/DSC and in-situ XRD results, the appropriate temperature for heat treatment was set to 700 °C, and the resulting samples were then subjected to the acid leaching in ascorbic acid.

Scanning electron microscopy (Fig. 4) was used to observe the morphology of the spent cathode active powder and its leaching residues. After the cell fade, the cathode materials, mostly $LiCoO_2$, showed irregular morphologies and contained large secondary particles with a wide particle size distribution. The leaching residue showed a much smaller particle size compared to that before leaching. EDX of the leaching residue (Fig. 5) indicated that it contained unleachable Co species, which is attributed to a cobalt oxide species (Co_3O_4 and CoO) resulting from the initial cell materials as well as the heat treatment.

3.2. Leaching of waste $LiCoO_2$

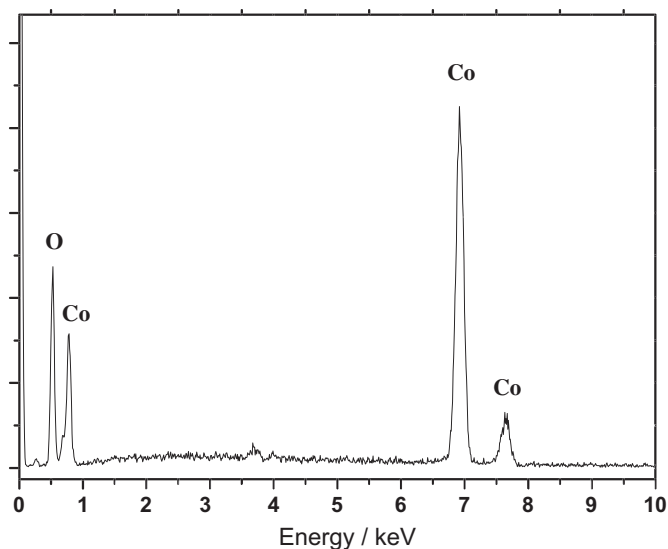Ascorbic acid behaves as a vinylogous carboxylic acid wherein the electrons in the double bond, hydroxyl group lone pair, and the carbonyl double bond form a conjugated system. Because the two major resonance structures stabilize the deprotonated conjugate base of ascorbic acid, the hydroxyl group in ascorbic acid is much more acidic than typical hydroxyl groups. In other words, ascorbic acid can be considered an enol in which the deprotonated form is a stabilized enolate. The pKa values of ascorbic acid as depicted in Fig. 6a is $pKa_1 = 4.10$ and $pKa_2 = 11.6$. In addition, ascorbic acid is also a mild reducing agent, which can be oxidized by one electron to a radical state or doubly oxidized to the stable form called dehydroascorbic acid ($C_6H_6O_6$), as shown in Fig. 6b.

During the leaching, the waste $LiCoO_2$ was first dissolved with ascorbic acid to form a soluble $C_6H_6O_6Li_2$, while Co^{3+} in $LiCoO_2$ was further reduced to a soluble Co^{2+} by the ascorbic acid. During the same time, the ascorbic acid ($C_6H_8O_6$) was oxidized to dehydroascorbic acid ($C_6H_6O_6$). Theoretically, there are several possible structures for the leaching products containing Co^{2+}, as listed in Fig. 7. However, simple thermodynamic calculation showed that only product (b), i.e., $C_6H_6O_6Co$, is thermodynamically favorable during the leaching [26]. The leaching reaction can, thus, be represented as follows:

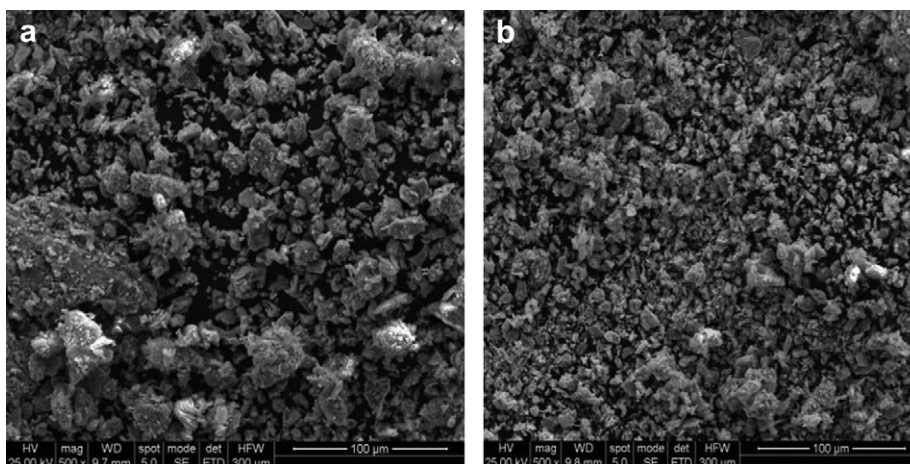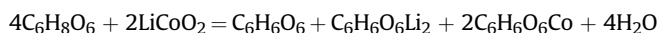$$4C_6H_8O_6 + 2LiCoO_2 = C_6H_6O_6 + C_6H_6O_6Li_2 + 2C_6H_6O_6Co + 4H_2O$$

Fig. 4. SEM micrographs of (a) dismantled cathode material from spent LIBs and (b) leach residues.
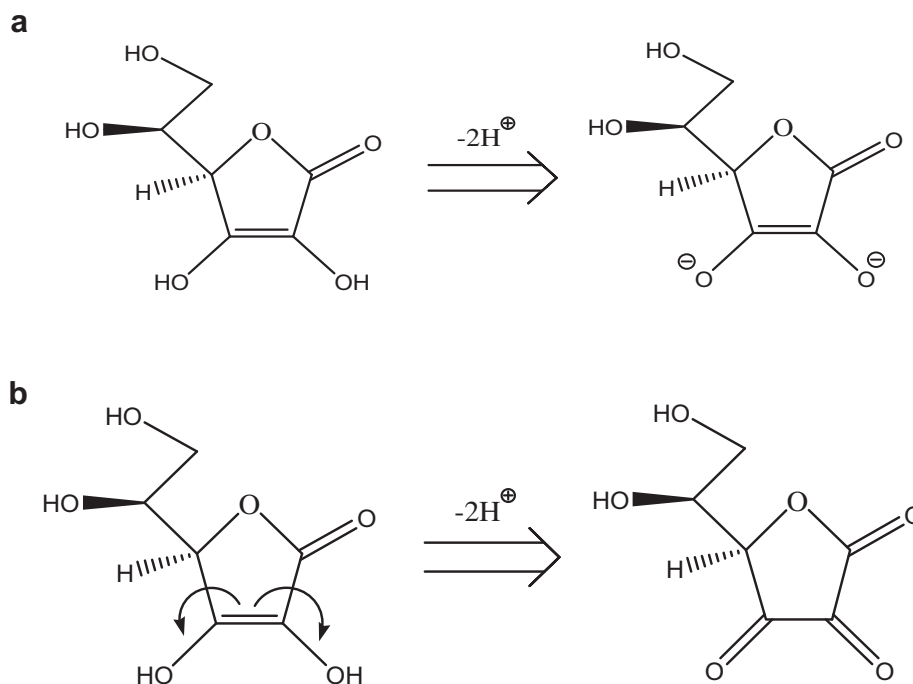
Fig. 6. The reaction of ascorbic acid as (a) organic acid and (b) reducing agent.

The efficiency of the acid-leaching process could be affected by several factors, such as leaching temperature and time, acid concentration, and S/L ratio. To optimize the operational conditions for the leaching of LiCoO$_2$, we conducted a series of experiments to investigate the influences of these factors.

3.2.1. Effect of temperature and time on leaching

The effect of the temperature and time on the leaching efficiency was studied by fixing the concentration of ascorbic acid at 1.25 mol L^{-1} and the S/L ratio at 25 gL^{-1}. The leaching was then carried out in the temperature range of 30–90 °C for 5–50 min. The leaching efficiency of cobalt and lithium was found to increase with increasing temperature (Fig. 8). Even at a low temperature of 30 °C, over 70% Co and 60% Li were leached, indicating that ascorbic acid is an effective leaching agent. With increased temperature to 70 °C,

the recovery was significantly improved, to 94.8% for Co and 98.5% for Li. Further increases of temperature did not improve the recovery of Co and Li, because ascorbic acid becomes unstable when the temperature is over 80 °C. The results in Fig. 8 also show that the influence of time on leaching efficiency is mainly in the early state of the leaching. As much as 79% Co and 89% Li could be leached in the first 5 min. With increasing the time to 20 min, the leaching efficiency improved to 94.8% for Co and 98.5% for Li. The leaching efficiency improved significantly when the time was further increased to 50 min.

3.2.2. Effect of ascorbic acid concentration on leaching

The concentration of ascorbic acid was found to play a key role in the leaching process. Increasing the amount of ascorbic acid was certainly beneficial to dissolving LiCoO$_2$, as it was for the leaching
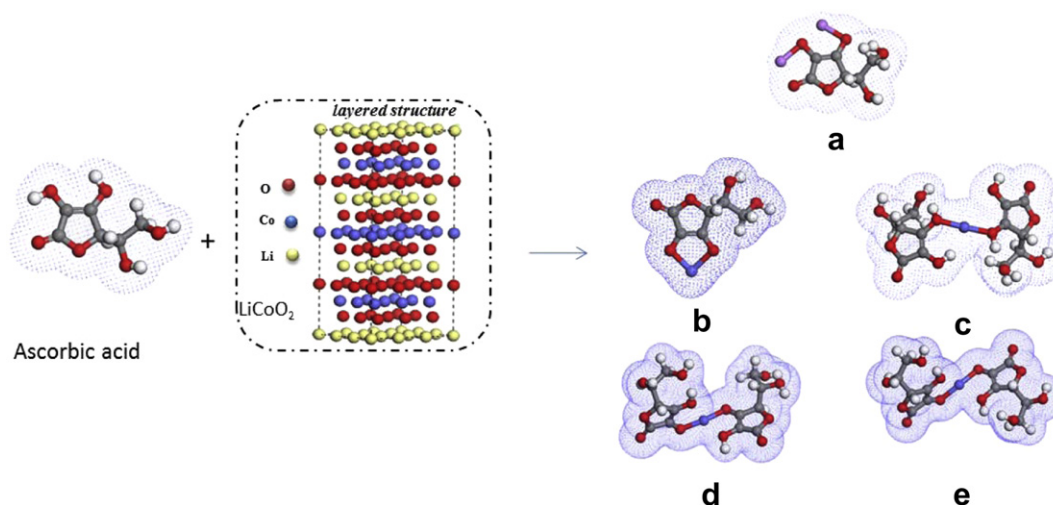

Fig. 7. Possible products of the leaching reaction of waste LiCoO$_2$ with ascorbic acid.
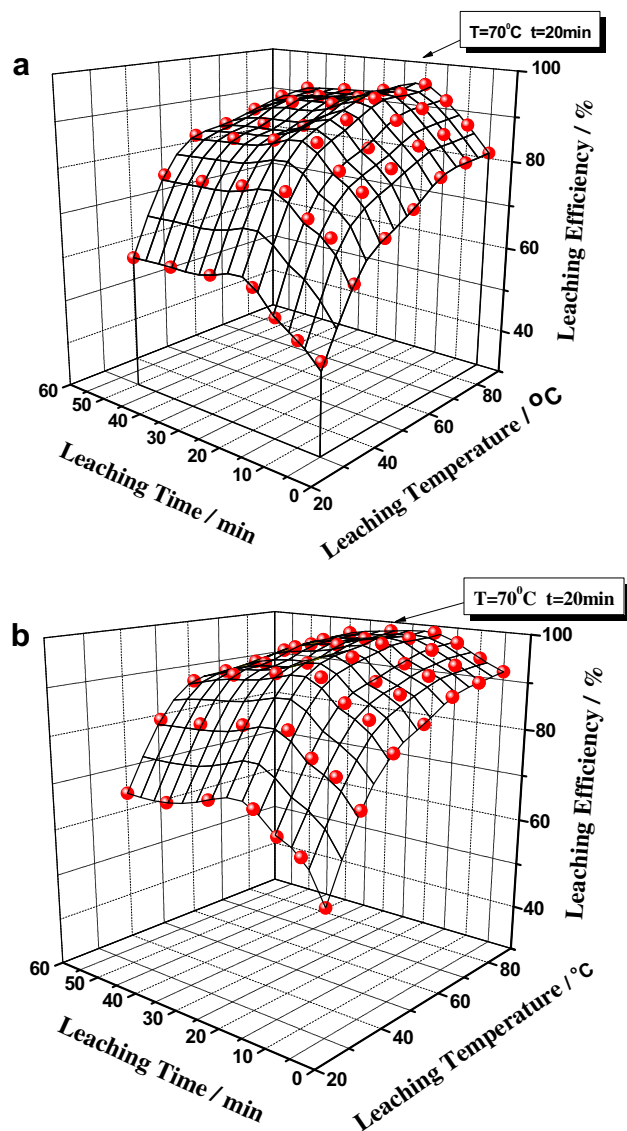
Fig. 8. Effect of temperature and time on the leaching efficiency of (a) cobalt and (b) lithium from waste LiCoO$_2$ ($t = 20$ min, $C = 1.25$ mol L^{-1}, $S/L = 25$ gL^{-1}, and agitation speed = 300 rpm).

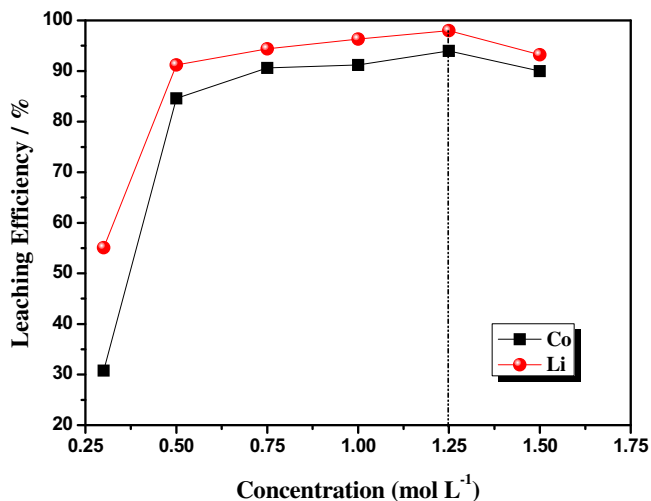**Fig. 9.** Effect of ascorbic acid concentration on the leaching of Co and Li from waste LiCoO$_2$ ($T = 70$ °C, $t = 20$ min, $S/L = 25$ gL^{-1}, and agitation speed = 300 rpm).
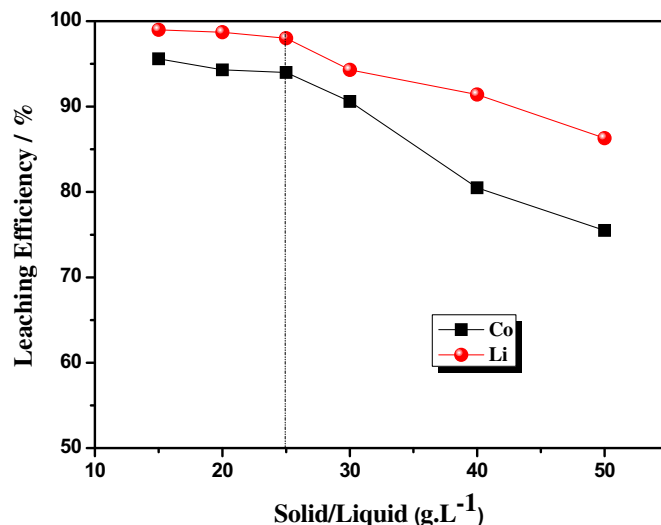

Fig. 10. Effect of solid/liquid ratio on the leaching of Co and Li from waste LiCoO$_2$ ($T = 70$ °C, $t = 20$ min, $C = 1.25$ mol L^{-1}, and agitation speed = 300 rpm).

efficiency. Fig. 9 shows the effect of the concentration of ascorbic acid on the leaching efficiency at 70 °C with an S/L ratio of 20 gL^{-1} and reaction time of 20 min. The leaching efficiency was only about 30.8% for Co and 55.1% for Li with the acid concentration at 0.3 mol L^{-1}. However, when the acid concentration reached 0.75 mol L^{-1}, the leaching efficiency increased significantly, i.e., to 90.6% for Co and 94.4% for Li. The highest leaching efficiency was achieved at the C$_6$H$_8$O$_6$ concentration of 1.25 mol L^{-1}, which resulted in about 94.8% and 98.5% recovery for Li and Co, respectively. Further increasing the C$_6$H$_8$O$_6$ concentration to 1.5 mol L^{-1} did not increase the leaching efficiency dramatically for either metal.

3.2.3. Effect of S/L ratio on leaching

Fig. 10 plots the effect of the S/L ratio on the leaching efficiency. For this experiment, the temperature was maintained at 70 °C, the leaching time was fixed at 20 min, and the C$_6$H$_8$O$_6$ concentration was fixed at 1.25 mol L^{-1}. From Fig. 10, one can clearly see that the leaching efficiency of both Co and Li decreased with increased S/L ratio. For example, the leaching efficiency dropped to 75.5% for Co and 86.3% for Li when the S/L ratio reached 50 gL^{-1}. In practice, a high S/L ratio is normally required to enhance the processing throughput, but this also leads to lower leaching efficiency. An S/L ratio of 25 gL^{-1} was suitable for both throughput and leaching efficiency. At this ratio, the leaching efficiency is about 94.8% for Co and 98.5% for Li.

4. Conclusions

A relatively simple and environmental friendly hydrome tallurgical-based process has been developed for the recovery of cobalt and lithium from spent LIBs. The physical pretreatments include discharging the battery and manually dismantling its components, followed by ultrasonic-assisted NMP immersion and calcination. The resulting LiCoO$_2$ powder was subjected to acid leaching. To avoid secondary pollution, organic ascorbic acid was chosen as the leaching reagent. Due to its reducibility, ascorbic acid can also replace H$_2$O$_2$ as the reducing agent. The optimum leaching conditions were determined to be ascorbic acid concentration of 1.25 mol L^{-1}, leaching temperature of 70 °C, leaching time of 20 min, and S/L ratio of 25 gL^{-1}. Under these experimental conditions, as much as 94.8% Co and 98.5% Li can be recovered at a relatively low

temperature in a short time. The leaching mechanism was also investigated from the viewpoint of the structure and chemical property of ascorbic acid. The test results demonstrated that the elimination of secondary pollution from strong acid can be achieved without decreasing the leaching efficiency. The whole recovery process is simpler and more environmentally friendly with low energy consumption compared with earlier methods.

References

[1] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, Energy Environ. Sci. 4 (2011) 3243.
[2] B. Scrosati, J. Hassoun, Y.K. Sun, Energy Environ. Sci. 4 (2011) 3287.
[3] S. Castillo, F. Ansart, C. Laberty-Robert, J. Power Sources 112 (2002) 247.
[4] Y. Pranolo, W. Zhang, C.Y. Cheng, Hydrometallurgy 102 (2010) 37.
[5] M.B.J.G. Freitas, V.G. Celante, M.K. Pietre, J. Power Sources 195 (2010) 3309.
[6] Michael J. Lain, J. Power Sources 97-98 (2001) 736.
[7] Jinqiu Xu, H.R. Thomas, Rob W. Francis, J. Power Sources 177 (2008) 512.
[8] D.A. Ferreira, L.M.Z. Prados, D. Majuste, J. Power Sources 187 (2009) 238.
[9] G. Dorella, M.B. Mansur, J. Power Sources 170 (2007) 210.
[10] P. Zhang, T. Yokoyama, O. Itabashi, Hydrometallurgy 47 (1998) 259.
[11] J. Nan, D. Han, X. Zuo, J. Power Sources 152 (2005) 278.
[12] B. Swain, J. Jeong, J. Lee, J. Power Sources 167 (2007) 536.
[13] M. Contestabile, S. Panero, B. Scrosati, J. Power Sources 92 (2001) 65.
[14] D. Mishra, Dong-Jin Kim, D.E. Ralph, Waste Management 28 (2008) 333.
[15] L. Li, J. Ge, F. Wu, J. Hazard. Mater. 176 (2010) 288.
[16] L. Li, J. Ge, Renjie Chen, Waste Manage. 30 (2010) 2615.
[17] C.K. Lee, K.I. Rhee, J. Power Sources 109 (2002) 17.
[18] D.C.R. Espinosa, A.M. Bernardes, J.A.S. Tenório, J. Power Sources 135 (2004) 311.
[19] O.A. Fouad, F.I. Farghaly, M. Bahgat, J. Anal. Appl. Pyrol. 78 (2007) 65.
[20] J.F. Paulino, N.G. Busnardo, J.C. Afonso, J. Hazard. Mater. 150 (2008) 843.
[21] G. Granata, E. Moscardini, F. Pagnanelli, F. Trabucco, L. Toro, J. Power Sources 206 (2012) 393.
[22] C. Bremus, U. Herrmann, S. Bringer-Meyer, J. Biotechnol. 124 (2006) 195.
[23] R.D. Hancock, R. Viola, Trends Biotechnol. 20 (2002) 299.
[24] http://www.mreza-upr.org/vitamin/vitamin-c-volatile.html.
[25] M.B.J.G. Freitas, E.M. Garcia, J. Power Sources 171 (2007) 953.
[26] G. S.Xu, H.M. WangLiu, L.J. Wang, H.F. Wang, J. Mol. Struct. Theochem. 809 (2007) 79.